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A Comparison of the Rates of Hydrolysis
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CARBARYL, PROPHAM AND CHLORPROPHAM: A COMPARISON OF THE RATES OF HYDROLYSIS AND PHOTOLYSIS WITH THE RATE OF BIOLYSIS

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Abstract—Alkaline hydrolysis half-lives, based on second-order alkaline hydrolysis rate constants, for carbaryl, protham (IPC), and chlorprotham (CIPC) at pH 9 (27°C) are $0.15 > 1 \times 10^4$, and $> 1 \times 10^4$ days, respectively. The direct photolysis half-life for carbaryl in sunlight is 6.6 days in distilled water. Calculated minimum half-lives for the direct photolysis of IPC and CIPC in a clear water body near the surface are 254 and 121 days, respectively. Half-lives, based on second-order fungal rate constants, for the IPC and CIPC are calculated under given conditions. Kinetic data on hydrolysis, photolysis, and biolysis are employed as a basis for comparison of the relative importance of these three degradation processes.

INTRODUCTION

Carbamate pesticides, esters of substituted carbamic

acid ($\text{H}_2\text{N}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{OH}$), are introduced into the environment through their application as both herbicides and insecticides. In general, the aryl esters of *N*-methyl substituted carbamic acids are insecticides. The addition of a second *N*-alkyl group results in a decrease in the insecticidal activity to some extent. On the other hand, the esters of *N*-aryl carbamic acid are selective herbicides for which varying the substituents on the *N*-aryl moiety affects the herbicidal activity. Thus, substitution of alkyl and aryl groups at both the nitrogen and oxygen atoms offers a diversity of herbicidal and insecticidal activity (Melnikov, 1971).

Carbamates find their way into the aquatic environment by several pathways such as application to soils followed by runoff or deposition of aerial mist (Kuhr & Dorrough, 1976). Also, carbamate herbicides are applied directly to natural waters in the control of aquatic weeds (Still & Herrett, 1976). Therefore, cognizance of the processes responsible for their degradation to non-biologically active products or transformation to other active compounds is imperative. Three such processes that require delineation are hydrolysis, photolysis, and biolysis. Moreover, as a result of the diverse structure and consequent large number of these environmental agents, it is desirable to be able to predict the persistence of these agents in aquatic ecosystems. For the hydrolytic process, the use of structure-reactivity relationships offers promise for predicting hydrolytic half-lives (Wolfe, 1977b).

The persistence of carbamate pesticides in soils has received much more attention than persistence in natural waters. Kazano *et al.* (1972) studied the degra-

dation of carbaryl (Fig. 1) (1-naphthyl *N*-methyl carbamate) and 3,5-xylyl *N*-methyl carbamate in five different soils. Persistence of the carbamate was influenced by soil type with 2–37% of theoretical carbon dioxide evolved in 32 days. Based on products, the authors concluded that hydrolysis was the predominant pathway of degradation. McClure (1972) investigated the breakdown of isopropyl *N*-phenyl carbamate (protham, IPC) and isopropyl *N*-(3-chlorophenyl)carbamate (chlorprotham, CIPC) (Fig. 1) in a sandy loam soil. The authors concluded that degradation was microbially mediated. In support of this microbial process, other investigators have isolated enzymes capable of hydrolyzing phenyl carbamates, and the mechanism of bond cleavage was determined based on product studies (Kearney & Kaufman, 1965). Thus, it appears that both hydrolysis and biolysis are viable degradation pathways in soils.

To evaluate the hydrolytic stability of four carbamate pesticides in water, Aly & El-Dib (1971a) carried out kinetic studies and calculated hydrolysis half-lives in distilled water at given temperatures and pH's. They concluded that the persistence of these carbamate pesticides in natural waters is greatly influenced by the pH and temperature of the aquatic environment.

Also, Faust & Gomaa (1972), in a review of the hydrolysis of pesticides in the aquatic environment,

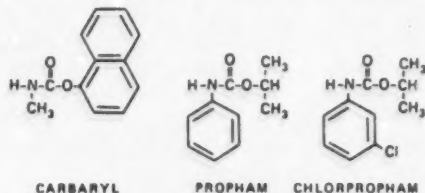


Fig. 1.

concluded that, under normal environmental pH's and temperatures, carbamates may be more persistent than presently recognized.

In this study, we have investigated the kinetics of hydrolysis and of photolysis for carbaryl, protham, and chlorprotham in water and compared the calculated half-lives with calculated half-lives for biolysis under a given set of conditions.

EXPERIMENTAL

All melting points were obtained on a Fisher Johns Melting Point Apparatus and are uncorrected.

Ultraviolet-visible absorption spectra were obtained on a Perkin-Elmer model 602 Digital Spectrophotometer.

Gas-liquid chromatographic (glc) analyses were carried out on a Tracor MT-220 gas chromatograph equipped with ^{63}Ni electron capture (EC) and flame ionization detectors (FID) and fitted with a 1.8 m $\times$ 3.5 mm i.d. column packed with 3% SE-30 on 80-100 mesh Chromosorb W. Gas chromatographic-mass spectrometric (gc-ms) analyses were performed with a Varian Aerograph model 1532-B gas chromatograph interfaced with a Finnigan 1015SL quadrupole mass spectrometer having a Gohlke glass jet separator and a Systems Industries 150 digital computer.

Liquid chromatographic (lc) analyses were carried out on either a Dupont 820 or a micromeritics 7000 liquid chromatograph employing ODS or Particil as the stationary phase and 45% methanol-water or isopropanol-octane as the respective mobile phase. Analyses were carried out using a u.v. detector at a wavelength of 254 nm, a pressure of 100 psi, and a flow rate of 2 ml min $^{-1}$.

(Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the U.S. Environmental Protection Agency.)

MATERIALS AND METHODS

Chemicals

(1) *Carbaryl*. Carbaryl was synthesized following the procedure of Skrabala & Young (1959) [mp 141-142°C, lit. 141-142°C].

(2) *Protham and chlorprotham*. Protham and chlorprotham were purified by column chromatography using silica gel as the sorbent and methylene chloride as the eluting solvent. Further purification was achieved by recrystallization from hexane; the melting points for protham and chlorprotham were 86-88°C [lit. 87-88°C, Moe (1970)] and 38-39°C [lit. 38-39°C, Moe (1970)], respectively.

(3) *N-Methyl-1-hydroxy-2-naphthamide*. The acid chloride of 1-hydroxy-2-naphthoic acid was prepared by refluxing the acid in thionyl chloride containing a trace of dimethylformamide. An ethereal solution of the acid chloride was slowly added to a stirred 1:1 mixture of ether and 40% aqueous methylamine with occasional cooling in an ice-water bath. The reaction mixture was neutralized by addition of concentrated hydrochloric acid, then the ether layer was washed with water, 5% aqueous sodium bicarbonate, and water. After drying over magnesium sulfate, the ether was removed under vacuum to yield the acid amide. Recrystallization from benzene-hexane yielded the pure amide [mp 122°C; Barr *et al.* (1961), mp 123-124°C].

(4) *N-Methyl-4-hydroxy-1-naphthamide*. The methyl ester of 4-hydroxy-1-naphthoic acid was prepared by a procedure described elsewhere (de Montmillan & Spieler, 1923). The ester was dissolved in 40% aqueous methylamine and the mixture was heated at 100°C for three days.

Upon cooling, the amide crystallized from the reaction mixture. Recrystallization from benzene-hexane gave white crystals [mp 177°C; de Montmillan & Spieler (1923), mp 178°C].

Chemical kinetic procedure

The procedure that was followed consisted of analyzing aliquots at given time intervals and has been described in detail elsewhere (Wolfe *et al.*, 1977; Wolfe *et al.*, 1976).

For carbaryl, the studies were carried out at 2×10^{-4} M in water at $27.00 \pm 0.02^\circ\text{C}$ buffered at pH 9.42 (boric acid-sodium hydroxide) or pH 4 (HCl) at $47.00 \pm 0.02^\circ\text{C}$. Aliquots were acidified with HCl and analyzed directly by lc as described above.

For IPC and CIPC, experiments were done using initial concentrations of 1×10^{-4} M and 1×10^{-5} M, respectively, in 0.15 M sodium hydroxide at $50.00 \pm 0.02^\circ\text{C}$ and $70.00 \pm 0.05^\circ\text{C}$ or pH 1 and $87.00 \pm 0.1^\circ\text{C}$. Analysis was performed by first extracting the sample with hexane and determining the change of concentration of the pesticide with time by glc analysis.

Product studies

Products were tentatively identified by comparison of lc or glc retention times of test samples with those of authentic samples. Confirmation was obtained by gc-ms.

Natural water studies

Natural water studies were carried out in water samples obtained from an eutrophic pond (Hickory Hills, pH 6.7) and an oligotrophic pond (USDA No. 1, pH 7.2), both located near Athens, GA. Sterile water samples were prepared by filtering through a 0.22 μm Millipore filter prior to use. Samples were taken aseptically during kinetic runs. At the end of the kinetic runs, sterility was rechecked (*Standard Methods*, 1965).

Photolytic studies

Photolytic studies for carbaryl were carried out either in sunlight in quartz tubes or at 313 nm wavelength light in Pyrex tubes at 4×10^{-4} M concentration in either air-saturated or degassed water. Quantum yields were determined in water at 313 nm employing a procedure described in detail elsewhere (Zepp *et al.*, 1975; Zepp *et al.*, 1976). Both kinetic and product studies were performed by direct analysis by lc as described above.

Organism and growth conditions

The fungus, *Aspergillus fumigatus*, was isolated from a local stream and identified by G. E. Michaels, Department of Microbiology, University of Georgia, using the scheme of Raper & Fennel (1965). Stock cultures of *A. fumigatus* were maintained on Sabouraud's medium (Difco) slants. Inocula for experiments were suspensions prepared by agitating 5 ml of sterile water in a tube containing the fungus. A pH 6.8 basal salts medium (Payne & Feisal, 1963) containing 0.05 g glucose l $^{-1}$ of distilled water was used on the liquid culture medium. Fungi were separated from liquid cultures for dry weight determinations by filtering first through tared prefilters then through tared 0.22 μm Nucleopore filters, and drying to a constant weight at 90°C.

Duplicate 500 ml flasks of the various weights of suspended fungi were prepared by measuring appropriate portions of liquid-medium inoculate with a fungal suspension. The flasks were then incubated on a gyrotory shaker at 28°C for 3 days. After incubation, cultures were adjusted to a final volume of 200 ml with a basal salts medium containing a predetermined amount of dissolved CIPC or IPC. Stock solutions of basal salts/herbicide were prepared by stirring herbicides overnight in the basal salts solution and filter-sterilizing through a 0.22 μm Millipore filter.

Table 1. Rate constants for the alkaline hydrolysis of carbaryl, protham, and chlorprotham in water

Compound	Temp °C	k, M ⁻¹ s ⁻¹	ΔH† Kcal/mol	ΔS† eu
Carbaryl	27	5.02 ± 0.03*	16.84 ± 0.01*	9 ± 2*
Protham	70	(2.6 ± 0.2) × 10 ⁻⁴	16.3 ± 0.2	-27 ± 1
	50	(5.6 ± 0.3) × 10 ⁻⁵		
	27§	7.6 × 10 ⁻⁶		
Chlorprotham	70	(6.4 ± 0.3) × 10 ⁻⁴	12.7 ± 0.2	-36 ± 1
	50	(1.9 ± 0.05) × 10 ⁻⁴		
	27§	2.0 × 10 ⁻⁵		

* Calculated from the data of Aly & El-Dib (1971) using their values of 16.9 Kcal/mole for the heat of activation.

† Rate constants were obtained by a least squares analysis of the data and the error is given as the standard deviation of error.

§ Extrapolated from elevated temperatures.

Fungal kinetics

Fungal concentrations in the medium were determined by dry weight. CIPC and IPC concentrations were determined by extracting a sample of the medium with 2,2,4-trimethylpentane (isooctane) and analyzing the extract by glc or lc. In the case of lc analysis, the concentration of the amine products was also determined.

DISCUSSION

To evaluate processes that determine the environmental persistence of carbaryl, protham, and chlorprotham (Fig. 1), the kinetics of their hydrolysis and direct photolysis were investigated in distilled water. Furthermore, we have extended the hydrolysis study to include natural water samples to allow for a comparison of half-lives predicted by laboratory data with that determined in natural water samples.

The measured second-order alkaline hydrolysis rate constants (k_{OH}) are given in Table 1 along with extrapolated values at 27°C. The activation parameters are also included to permit convenient extrapolation of the rate constants to other temperatures.

Rate constants for the acid catalyzed contribution (k_H) and for the neutral contribution (k_{H_2O}) were not determined because preliminary experiments indicated hydrolysis by these pathways was too slow to be of environmental significance. Minimum values were established from screening experiments, as follows. For carbaryl, no degradation was detected after 10 days at 47°C and pH 5. By assuming an error of 10% in the analysis, a maximum pseudo-first-order

rate constant is calculated to be $5 \times 10^{-8} s^{-1}$ at 47°C. Assuming a change of a factor of 10 in the rate constant for a 20° change in temperature (Aly & El-Dib, 1971a) gives an estimated rate constant of $5 \times 10^{-9} s^{-1}$ at 27°C, which corresponds to a minimum half-life of 1.6×10^3 days. Protham and chlorprotham were even less reactive than carbaryl. At 87°C and pH 1 after 10 days, no change in pesticide concentration was detected. Based on these data, the acid-catalyzed and neutral hydrolysis pathways can be disregarded under environmental reaction conditions. Thus, the half-life expression for all three compounds becomes

$$t_{1/2} = (0.693/k_{OH} [OH^-]) \quad (1)$$

where k_{OH} is the second-order alkaline hydrolysis rate constant and $[OH^-]$ is the hydroxide ion concentration.

The mechanism for alkaline hydrolysis has been investigated for *N*-alkyl and *N*-aryl carbamates (Bender & Homer, 1965; Christenson, 1964). The reaction pathway, at least in the case of a reactive *N*-alkyl carbamate like carbaryl, is shown in Fig. 2.

For carbaryl hydrolysis 1-naphthol was identified as the major product. Methyl isocyanate which is believed to be formed is not stable under alkaline reaction conditions and is readily hydrolyzed to methyl amine. In the case of IPC and CIPC, aniline and *m*-chloroaniline were identified as breakdown products. This dictates that isopropyl alcohol should also be a product.

Natural water studies

Carbaryl and protham were added to Hickory Hills (pH 6.7) and USDA No. 1 (pH 7.2) pond waters. For carbaryl, the experimentally determined half-life of 30 days for Hickory Hills pond water compared with the calculated half-life of 32 days. For USDA No. 1 pond water, the experimental and calculated values were 12 days and 10 days, respectively. Natural water studies with chlorprotham were carried out at elevated temperatures. At 67°C chlorprotham showed no change in concentration in either water sample after 1 week, a result that agrees with the predicted rate. These results suggest that there is no catalytic

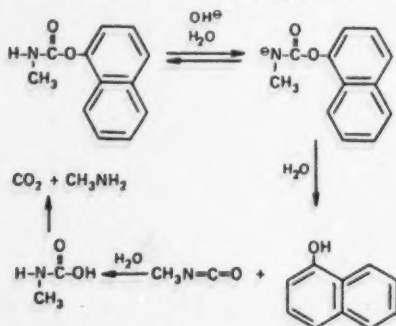


Fig. 2.

Table 2. Quantum yields for photolysis of carbaryl at 25 °C (313 nm) in water

Reaction conditions	Disappearance quantum yields
Degassed, pH 5.5	0.016
Air-saturated, pH 5.5	0.0056
Air-saturated, pH 5.2	0.0052
Air-saturated, pH 6.1	0.0058
Air-saturated, pH 6.9	0.0055

effect in these natural waters and that the calculated results based on laboratory data can be used to predict the hydrolysis contribution of dissolved carbamates in natural waters.

Photolysis

Preliminary studies with carbaryl, propham, and chlorpropham indicated that carbaryl would photolyze rapidly under sunlight. On the other hand, propham and chlorpropham would photolyze very slowly. Therefore, detailed photolytic rate studies were limited to carbaryl. Estimates of the minimum photolytic half-life of propham and chlorpropham in distilled water are included for comparison, however.

Quantum yields for carbaryl measured at 313 nm in water are given in Table 2. These data indicate that photolysis is slowed by the presence of oxygen but is independent of pH over the limited pH range studied. Although the quantum yield is quite low, carbaryl does adsorb sunlight rapidly and photodegrades easily. Experiments under June midday sunlight (lat. 34°N) in distilled water at pH 5.5 gave a half-life of 45 h. Dark controls showed no decomposition. Based on the method of Zepp and coworkers (Zepp *et al.*, 1976; Zepp & Cline, 1977), the calculated half-life for direct photolysis is about 50 h in a clear water body near the surface. This method employs the experimentally determined quantum yield, the u.v.-vis absorptivity over sunlight wavelengths, and average daily sun-

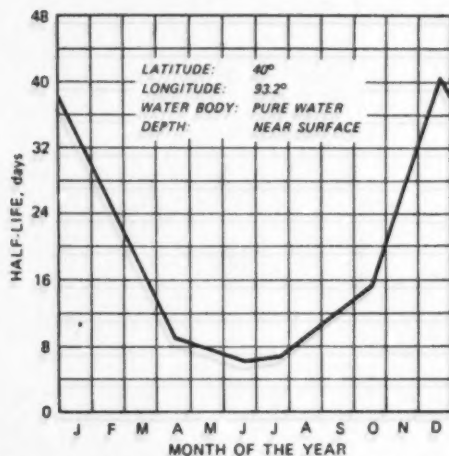


Fig. 3. Calculations of the annual variation of the photolysis half-life of carbaryl with the seasons of the year.

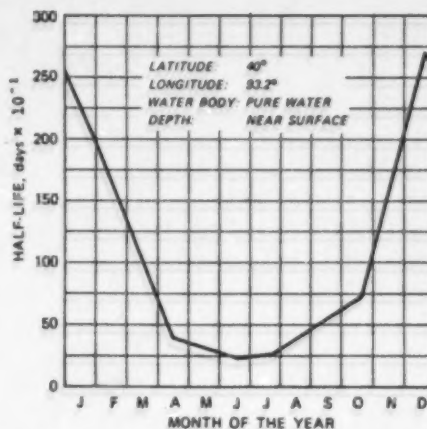


Fig. 4. The annual variation of the photolysis half-life for propham.

light solar intensities. Figure 3 shows calculations of the annual variation of the photolysis half-life of carbaryl with the seasons of the year. It is noteworthy that, in the spring and summer when carbaryl is applied, photolysis is about four times faster than in the winter months.

Because screening studies showed that propham and chlorpropham underwent direct photolysis very slowly in distilled water, quantum yields were not determined. A minimum direct photolysis half-life can be calculated, however, assuming a quantum yield of 1. Using the model of Zepp and coworkers (1976, 1977) gives a calculated minimum half-life of 254 days for propham and 121 days for chlorpropham. Figure 4 shows the annual variation of the photolysis half-life for propham and, though not shown, chlorpropham exhibits a similar seasonal variation. These data indicate that even during the spring and summer months, these two carbamates slowly undergo direct photolysis.

Photolysis product studies

Reported products for this direct photolysis of carbaryl are 1-naphthol and methyl isocyanate along with other unidentified cholinesterase inhibitors (Crosby *et al.*, 1965). Aly & El-Dib (1971a) reported that carbaryl photolyzed to give 1-naphthol and that 1-naphthol in alkaline, air-saturated water photolyzed to give 2-hydroxy-1,4-naphthoquinone. Other studies indicate that aryl carbamates may undergo a photo-reaction similar to the photo-Fries type rearrangement. Therefore, *N*-methyl-1-hydroxy-2-naphthamide and *N*-methyl-4-hydroxy-1-naphthamide, both potential carbaryl photoproducts, were synthesized (Silk & Unger, 1973; Kumar *et al.*, 1974; Addison *et al.*, 1974; Addison *et al.*, 1973).

A careful product study did not reveal any of the above products. However, they can be characterized as non-volatile; even methylation (diazomethane) produced no products detectable by glc. Also, highly col-

ored products that formed in air-saturated water were absent in air free water. One possible explanation would be the formation of non-volatile, high molecular weight products by polymerization.

Biolysis

During the course of laboratory experiments with IPC and CIPC, no growth of fungi could be detected. Fungal biomass was regarded as constant, therefore, and a constant enzyme concentration was assumed for the duration of the experiments.

Herbicide transformation for a given fungal concentration was first order with respect to herbicide concentrations from 3.0 to 40 mg l⁻¹ for IPC and from 2.0 to 25 mg l⁻¹ for CIPC.

The observed velocities of IPC and CIPC transformations can be accurately described using the Michaelis-Menton expression (White *et al.*, 1964).

$$V = \frac{V_{\max}[S]}{K_m + [S]} \quad (2)$$

where $V_{\max}$ is the maximum velocity of CIPC or IPC uptake, $[S]$ is herbicide concentration, and K_m is the Michaelis-Menten constant or concentration of herbicide for one-half maximal velocity.

Using a rearranged form (Lineweaver & Burke, 1934) of the above equation

$$\frac{[S]}{V} = \frac{[S]}{V_{\max}} + \frac{K_m}{V_{\max}} \quad (3)$$

experimental values of $1/V$ were plotted as a function of $1/[S]$. The Y intercepts of the resulting plots, $1/V_{\max}$, which were determined by least squares analysis, yield values for $V_{\max}$ of $(1.8 \pm 0.4) \times 10^{-3}$ mg IPC mg⁻¹ fungus h⁻¹ and $(3.8 \pm 0.8) \times 10^{-3}$ mg CIPC mg⁻¹ fungus h⁻¹. K_m values were determined from the slopes, $K_m/V_{\max}$, to be 150 ± 35 μ mol IPC l⁻¹ and 46 ± 9 μ mol CIPC l⁻¹.

Assuming a constant ratio of enzyme activity to fungal biomass and using equation (2), the removal of IPC and CIPC may be described by

$$-\frac{d[S]}{dt} = \frac{V_{\max}[S]}{K_m + [S]} [F] \quad (4)$$

where $[F]$ is mg (dry weight) of fungi l⁻¹ medium.

At substrate concentrations much, much lower than the K_m values, equation (4) reduces to

$$-(d[S]/dt) = k[S][F]. \quad (5)$$

Table 3. Rate constants (k) for microbial degradation of herbicides

Microorganisms	CIPC	IPC
	k $l(\text{mg M}^{-1})^{-1} \text{ h}^{-1}$	
<i>Pseudomonas striata</i> †	1×10^{-1}	9×10^{-2}
<i>Aspergillus fumigatus</i>	2.5×10^{-4}	1.5×10^{-4}

* Dry weight (mg) of microorganisms.

† Moe (1970).

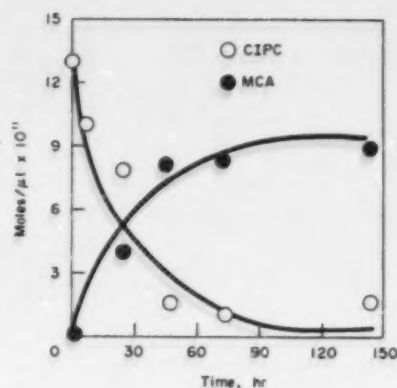


Fig. 5. Rate profile for the disappearance of CIPC and the formation of MCA.

Table 3 contains the second-order rate constants for IPC and CIPC. Although not shown here, studies over the pH range of 5–8 indicated no pH effects, a result that is in contrast to what Kearney & Kaufman (1965) observed in their enzyme studies.

Rate constants for the formation of aniline and *m*-chloroaniline were the same as rate constants for the disappearance of IPC and CIPC (Fig. 5) indicating that hydrolysis of the ester bond is the initial step in the fungal degradation of the herbicides. Degradation of aniline and *m*-chloroaniline was not detected one week after their initial formation.

Moe (1970) determined rates of bacterial degradation of these herbicides. In his studies, *Pseudomonas striata* used the herbicides as primary carbon sources for growth. Concentrations of the herbicides used in Moe's studies were high; the growth rate constants were maximum in all experiments. To compare the degradation rates in the bacterial and fungal systems, values of the second-order rate constants for the bacteria were calculated from Moe's data for a temperature of 30 °C (Table 3). Rate constant values for the bacterial cultures are two orders of magnitude higher than rate constant values for the fungal cultures. Similar findings have been reported earlier by our Laboratory (Lewis *et al.*, 1975) in malathion degradation studies. In these investigations, a mixed bacterial population degraded malathion 5000 times faster than the same weight of fungi under similar conditions of malathion concentration, temperature, and agitation rate.

Comparison of hydrolysis and direct photolysis with biolysis

A comparison of hydrolysis and direct photolysis half-lives with biolysis half-lives for carbaryl, propham, and chlorpropham is difficult because most biological studies are conducted under environmental conditions that preclude the determination of rate constants. Recent studies by Paris and coworkers, however, have provided a limited amount of data. One such study determined the kinetics of degrada-

Table 4. Comparison of calculated hydrolysis, photolysis, and biolysis half-lives under given conditions

Compound	pH	Hydrolysis half-life, days*	Direct photolysis half-life, days	Biolysis half-life, days	
				Fungi	Bacteria
Carbaryl	5	1500	6.6	—	$> 3 \times 10^{4\dagger}$
	7	15	6.6	—	—
	9	0.15	—	—	—
IPC	5	$> 1 \times 10^4$	254‡	—	—
	7	$> 1 \times 10^4$	254	190§	3.2††
	9	$> 1 \times 10^4$	254	—	—
CIPC	5	$> 1 \times 10^4$	121	—	—
	7	$> 1 \times 10^4$	121	120§	2.9††
	9	$> 1 \times 10^4$	121	—	—

* Hydrolysis half-lives calculated based on neutral and alkaline hydrolysis assuming pseudo-first-order kinetics.

† Minimum value assuming a bacterial population of 0.1 mg l^{-1} .

‡ Minimum direct photolysis half-lives calculated by the procedures of Zepp & Cline (1977) assuming a quantum efficiency of 1 and for a mid-summer day at latitude 40° .

§ Calculated assuming 1 mg l^{-1} fungi.

†† Calculated from the data of Moe (1970).

tion of carbaryl by a heterogeneous bacterial population obtained from natural waters (Paris *et al.*, 1975). In this study, the microorganisms did not degrade carbaryl but did utilize the 1-naphthol that was formed as a result of hydrolysis. Using these data and assuming a 10% error in carbaryl analysis, we have calculated a maximum value of $1 \times 10^{-14} \text{ l org}^{-1} \text{ h}^{-1}$ for the second-order rate constant.

Data for the three processes are summarized in Table 4 for a given set of reaction conditions. Based on these data, carbaryl would be non-persistent in the aquatic environment. At pH's greater than 7, hydrolysis will contribute to its degradation but below pH 6, it will be negligible. Direct photolysis half-lives, however, are very short and photolysis would contribute significantly under certain environmental conditions. Based on the data for bacterial degradation by naturally occurring aquatic populations, biodegradation is unlikely to be fast enough to compete as a degradation pathway.

These data also show that hydrolysis and photolysis are very slow for protham and chlorprotham. The very limited data also suggest that fungal degradation will be quite slow. On the other hand, bacterial degradation appears to be quite fast and may be the dominant degradation pathway for IPC and CIPC under certain environmental conditions.

Although the transformation half-lives reported for biolysis, photolysis, and hydrolysis are not expected to be the same as predicted on the basis of these few experiments, these data do provide some logical bases for comparison of the relative importance of these three processes.

SUMMARY

Rate constants for alkaline hydrolysis, direct photolysis, and biolysis indicate that hydrolysis and photolysis will be competitive degradation pathways for carbaryl. For IPC and CIPC, the short half-lives

for bacterial degradation indicate that biolysis will be the most competitive degradation process.

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